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Date of Deposit

Form PTO-1390 (REV 10-95)		U. S. Department of Commerce Patent and Trademark Office		ATTORNEY'S DOCKET NUMBER CO/2-22109/A/PCT	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
				10/088222	
INTERNATIONAL APPLICATION NO. EP 00/10043		INTERNATIONAL FILING DATE October 12, 2000		PRIORITY DATE CLAIMED October 20, 1999	
TITLE OF INVENTION PHOTOINITIATOR FORMULATIONS					
APPLICANT(S) FOR DO/EO/US Manfred Köhler (deceased), Beat Michael Aebli, Martin Holer and Ernst Eckstein					

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau. (**See attached Form PCT/IB/308**)
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English 35.U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included.

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: (**See attached Form PCT/ISA/210**)

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 10/088222		INTERNATIONAL APPLICATION NO. EP 00/10043		ATTORNEY'S DOCKET NUMBER CO/2-22109/A/PCT	
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17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(5)):					
Search Report has been prepared by the EPO or JPO \$890.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482) \$710.00					
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)). \$740.00					
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. \$1040.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath of declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	18 - 20 =	0	X \$18.00	\$	
Independent claims	1 - 3 =	0	X \$84.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00 \$	
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	
TOTAL FEES ENCLOSED =				\$	
				Amount to be: refunded \$	
				charged \$890.00	

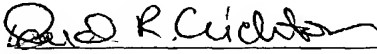
a. ☒ Please charge my Deposit Account No. 03-1935 in the amount of \$890.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

b. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-1935. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

PLEASE ASSOCIATE THE ATTACHED APPLICATION WITH CUSTOMER NUMBER 000324 AND SEND ALL CORRESPONDENCE TO:

JoAnn Villamizar
Patent Department
540 White Plains Road
P.O. Box 2005
Tarrytown, NY 10591-9005


 SIGNATURE

 NAME: **David R. Crichton**

 REG. NO. 37,300

10/088222

Photoinitiator formulations

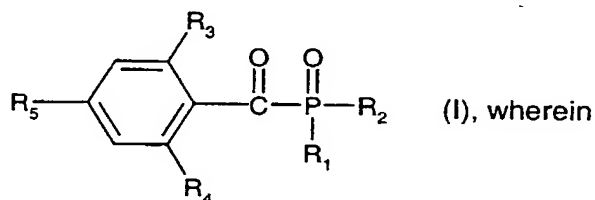
The present application relates to aqueous suspensions of photoinitiators and to the preparation and use thereof.

It is known in the art to add additives in dispersed form, that is to say in the form of emulsions or suspensions, to polymerisable formulations, especially in order to facilitate incorporation of the additives into those formulations. The additives are for that purpose usually homogeneously dissolved in one phase or melted with one another and then dispersed in water.

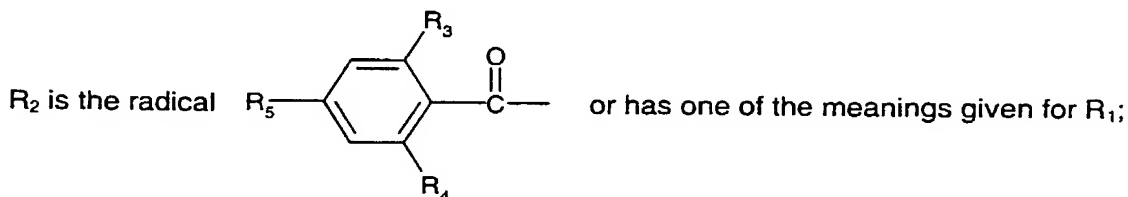
For example, in US 5 196 142 and US 5 116 534 aqueous emulsions of antioxidants are described and in US 5 549 847 aqueous dispersions of corrosion inhibitors are disclosed. Published in US 4 965 294 and US 5 168 087 are aqueous emulsions of photoinitiators, especially hydroxyketones.

There is a need in the art for effective, stable photoinitiators that can readily be incorporated.

The invention relates to aqueous, storage-stable, non-sedimenting suspensions comprising (a) at least one mono- or bis-acylphosphine oxide of formula I



R_1 is C_1 - C_{20} alkyl; C_2 - C_{20} alkyl interrupted by one or more O atoms; C_1 - C_{12} alkoxy; phenyl- C_1 - C_4 alkyl; or phenyl that is unsubstituted or substituted by C_1 - C_{20} alkyl, C_1 - C_{12} alkoxy, halogen, cyclopentyl, cyclohexyl, C_2 - C_{12} alkenyl, C_2 - C_{18} alkyl interrupted by one or more O atoms, and/or by phenyl- C_1 - C_4 alkyl; or R_1 is biphenyl;



R_3 and R_4 are each independently of the other C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy or halogen; and

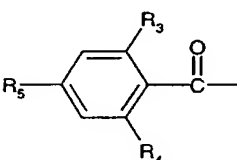
Phenyl-C₁-C₄alkyl is phenyl-substituted C₁-C₄alkyl and is, for example, benzyl, phenylethyl, α -methylbenzyl, phenylpropyl or α,α -dimethylbenzyl, especially benzyl. Phenyl-C₁-C₂alkyl is preferred.

Halogen is fluorine, chlorine, bromine or iodine, especially chlorine or bromine, preferably chlorine.

C₂-C₁₂Alkenyl radicals may be mono- or poly-unsaturated and linear or branched and are, for example, C₂-C₈-, C₂-C₆- or C₂-C₄-alkenyl. Examples are allyl, methallyl, 1,1-dimethylallyl, 1-butenyl, 2-butenyl, 1,3-pentadienyl, 1-hexenyl, 1-octenyl, decenyl and dodecenyl, especially allyl. R₁ as C₂-C₁₂alkenyl is, for example, C₂-C₈-, C₂-C₆- or, especially, C₂-C₄-alkenyl.

R₁ as substituted phenyl is mono- to penta-substituted, for example mono-, di- or tri-substituted, especially mono- or di-substituted, on the phenyl ring.

Preferred substituents for R₁ as substituted phenyl are C₁-C₄alkyl, especially methyl, and C₁-C₆alkoxy, especially pentyloxy and methoxy.

When R₂ is the radical , the meanings of R₃, R₄ and R₅ in that radical do

not necessarily have to be identical to those of the radicals R₃, R₄ and R₅ in the other benzoyl group in the compound of formula I, that is to say, suitable compounds of formula I also include asymmetrical bisacylphosphine oxides.

The expression "and/or" in relation to the definition of the present invention indicates that not only one of the defined alternatives (substituents) but several different defined alternatives (substituents) may be present together, that is to say, mixtures of different alternatives (substituents) may be present.

The expression "at least one" defines "one" or "more than one", for example one, two or three, preferably one or two.

The preparation of the compounds of formula I is known to the person skilled in the art and is widely described in the literature. For example, corresponding processes are described in the following specifications: US 4 737 593, US 4 792 632, US 5 218 009, US 4 298 738, US 5 504 236, US 5 399 770, US 5 767 169.

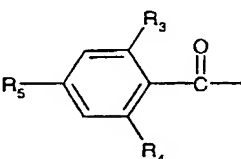
For example, compounds of formula I having two benzoyl groups (bisacylphosphine oxides) can be prepared, for example, by double acylation of a primary phosphine using at least two equivalents of an acid chloride in the presence of at least two equivalents of a base, and subsequent oxidation of the resulting diacylphosphine. The reaction conditions can be obtained from the above-mentioned literature sources.

The monoacylphosphine oxides can be obtained in an analogous manner.

Some of the compounds of formula I are also obtainable commercially, such as, for example, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (^{RTM}Lucirin TPO, BASF); bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (^{RTM}Irgacure 819, Ciba Spezialitätenchemie) and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (as ^{RTM}Irgacure 1700, ^{RTM}Irgacure 1800 and ^{RTM}Irgacure 1850 in admixture with α -hydroxyketones from Ciba Spezialitätenchemie).

In the suspensions according to the invention, preference is given to the compounds of formula I wherein

R₁ is C₁-C₂₀alkyl; C₁-C₄alkoxy; or phenyl that is unsubstituted or substituted by C₁-C₁₂alkyl, C₁-C₁₂alkoxy and/or by halogen;

R₂ is the radical  or has one of the meanings given for R₁;

R₃ and R₄ are each independently of the other C₁-C₄alkyl or C₁-C₄alkoxy; and
R₅ is hydrogen, C₁-C₁₂alkyl or C₁-C₁₂alkoxy.

Preference is given also to an aqueous suspension comprising as component (a) a compound of formula I wherein

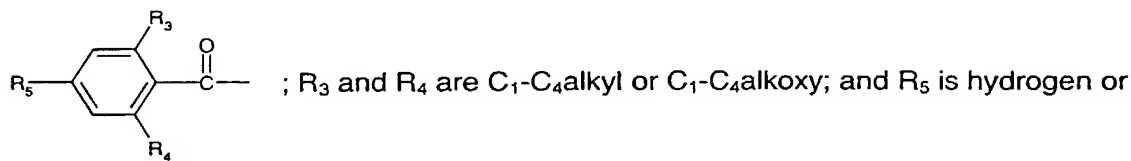
R₁ is C₁-C₂₀alkyl; C₂-C₂₀alkyl interrupted by one or more O atoms; benzyl; or phenyl that is unsubstituted or substituted by C₁-C₂₀alkyl, C₁-C₁₂alkoxy and/or by halogen;

Photoinitiators in solid physical form, especially, are used in the suspensions according to the invention.

It will be understood that the suspensions according to the invention may also comprise a plurality of compounds of formula I. For example, suspensions comprising a monoacylphosphine oxide in combination with a bisacylphosphine oxide or comprising a plurality of bisacylphosphine oxides are of interest, for example mixtures of 2,4,6-trimethylbenzoyldiphenylphosphine oxide and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide or 2,4,6-trimethylbenzoyldiphenylphosphine oxide and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide or bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide.

Preferred suspensions according to the invention are those wherein

(a) is a compound of formula I wherein R_1 is phenyl or C_1 - C_{12} alkyl; R_2 is



C_1 - C_4 alkyl; and

(b) is an alkali salt of a carboxylic acid polymer, or is polyvinyl alcohol or a modified polyacrylate.

Suitable dispersants (b) are all surface-active compounds, preferably anionic and non-ionic surfactants and polymeric dispersants. The following classes of compounds are examples of the dispersants that can be used according to the invention:

1. Anionic surfactants

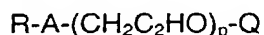
1.1 Condensates of aromatic sulfonic acids with formaldehyde, such as condensation products of formaldehyde and naphthalenesulfonic acid or of formaldehyde, naphthalene sulfonic acid and benzenesulfonic acid, or condensation products of crude cresol, formaldehyde and naphthalenesulfonic acid.

1.2 Lignosulfonates, for example those obtained by the sulfite or kraft process. Preferably these are products some of which are hydrolysed, oxidised or desulfonated and fractionated by known processes, for example according to molecular weight or the degree of sulfonation. Mixtures of sulfite- and kraft-lignosulfonates are very effective.

1.3 Dialkyl sulfosuccinates in which the alkyl moieties are branched or unbranched, for example dipropyl sulfosuccinate, diisobutyl sulfosuccinate, diamyl sulfosuccinate, bis(2-ethyl hexyl)sulfosuccinate or dioctyl sulfosuccinate.

1.4 Sulfated or sulfonated fatty acids or fatty acid esters of fatty acids, for example sulfated oleic acid, elaidic acid or ricinolic acid and the lower alkyl esters thereof, for example the ethyl, propyl or butyl esters. Also very suitable are the corresponding sulfated oils, such as olive oil, rapeseed oil and, especially, castor oil.

1.5 Reaction products of ethylene oxide and/or propylene oxide with saturated or unsaturated fatty acids, fatty alcohols, fatty amines, alicyclic alcohols or aliphatic-aromatic hydrocarbons that are terminally esterified with an inorganic oxygen-containing acid or a polybasic carboxylic acid. Such compounds are preferably compounds of formula



wherein R is an aliphatic hydrocarbon radical having from 8 to 22 carbon atoms or a cycloaliphatic or aliphatic-aromatic hydrocarbon radical having from 10 to 22 carbon atoms; A is -O-, -NH- or -CO-O-; Q is the acid radical of an inorganic, polybasic acid or the radical of a polybasic carboxylic acid and p is a number from 1 to 20, preferably from 1 to 5. The radical R-A- is derived, for example, from a higher alcohol, such as decyl alcohol, lauryl alcohol, tridecyl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, arachidyl alcohol, hydroabietyl alcohol or behenyl alcohol; from a fatty amine, such as stearylamine, palmitylamine or oleylamine; from a fatty acid, such as caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, coconut fatty (C₈-C₁₈) acid, decenoic acid, dodecenoic acid, tetradecenoic acid, hexadecenoic acid, oleic acid, linoleic acid, linolenic acid, eicosenoic acid, docosenoic acid or clupanodonic acid; or from an alkylphenol, such as butylphenol, hexylphenol, n-octylphenol, n-nonylphenol, p-tert-octylphenol, p-tert-nonylphenol, decylphenol, dodecylphenol, tetradecylphenol or hexadecylphenol.

The acid radical Q is normally derived from a low-molecular-weight dicarboxylic acid, such as maleic acid, malonic acid, succinic acid or sulfosuccinic acid, and is linked by way of an ester bridge to the radical R-A-(CH₂CH₂O)_p-. Preferably, however, Q is derived from an inorganic polybasic acid, such as orthophosphoric acid or sulfuric acid. The acid radical Q is preferably in salt form, for example in the form of an alkali metal salt, ammonium salt or amine salt. Examples of such salts are sodium, potassium, ammonium, trimethylamine, ethanolamine, diethanolamine and triethanolamine salts.

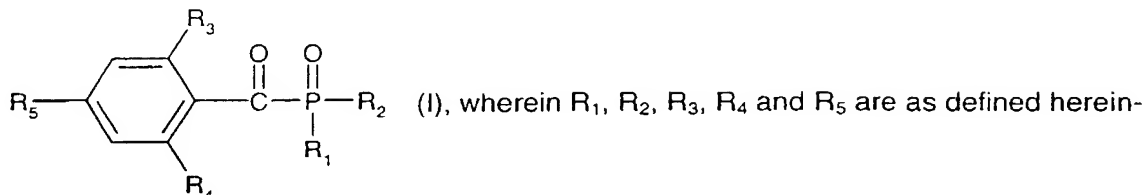
Suitable polymeric dispersants include, for example, amphiphilic copolymers, block copolymers and graft or comb polymers, especially those based on acrylic acid, methacrylic acid or salts thereof, hydroxyalkyl(meth)acrylic acid, aminoalkyl(meth)acrylic acid or salts thereof.

In addition to the dispersant and the thickener, the suspensions according to the invention may contain further adjuvants (d), such as hydrotropic agents, for example urea or sodium xylenesulfonate; antifreeze agents, such as ethylene glycol or propylene glycol, diethylene glycol, glycerol or sorbitol; humectants, such as polyethylene glycols or glycerol; biocides, such as chloroacetamide, formalin or 1,2-benzisothiazolin-3-one; or chelating agents, such as trisodium nitrilotriacetate.

The amount of component (a) in the photoinitiator suspension according to the invention is, for example, from 10 to 80 parts or from 20 to 70 parts, especially from 10 to 50 parts, e.g. from 25 to 45 parts, preferably from 40 to 50 parts, e.g. from 40 to 45 parts. Component (b) is added to the suspension, for example, in an amount of from 0.1 to 40 parts, from 0.1 to 10

After the first step of mixing the components, the mixture is, for example, coarsely ground in a further step (2). For that purpose the mixture is introduced into appropriate grinders. Suitable grinders for the grinding step, and for the grinding steps described hereinbelow, are generally known to the person skilled in the art. Suitable grinders for step (2) include, for example, toothed colloid mills, for example those from Fryma (Rheinfelden, Switzerland) which operate according to the stator/rotor principle. "Coarsely ground" in this context indi-

(a) at least one mono- or bis-acylphosphine oxide of formula I



before,

(b) at least one dispersant,

(c) water, and, optionally,

(d) further additives

by

(1) suspending components (a), (b) and (c) and, optionally, (d), by stirring;

(2) coarse-grinding the resulting mixture to a particle size of the solid material in the suspension of approximately 60 μm ; and

(3) fine-grinding the mixture by one or more grinding operations to a particle size of the solid material in the suspension of less than 12 μm .

Depending on the constituents used, the suspension may already have the desired particle size distribution or stability after the stirring operation. In such cases steps (2) and (3) are superfluous to the preparation of suspensions according to the invention.

The suspensions according to the invention so obtained are storage-stable for a long time at room temperature and can very readily be incorporated in that form into aqueous formulations that are to be polymerised. They comprise the photoinitiator in a heterogeneous phase, that is to say not dissolved in a constituent of the formulation but in solid form.

For use of the suspensions in aqueous media, it is of advantage that they can be handled as fluids and, for example, can be pumped for metered addition.

Despite the aqueous medium, the mono- and bis-acylphosphine oxide compounds present therein remain stable and reactive.

In accordance with the invention, the suspensions of the acylphosphine oxide compounds can be used as photoinitiators in the photopolymerisation of compounds having ethylenic unsaturation or of mixtures comprising such compounds.

Such use can also be carried out in combination with another photoinitiator. Preferably, however, the suspension according to the invention is used as the sole photoinitiator.

The invention accordingly relates also to photopolymerisable compositions comprising

(A) at least one ethylenically unsaturated photopolymerisable compound and

(B) as photoinitiator, a suspension as described above,

it being possible for the composition to contain, in addition to component (B), further additives (C).

The unsaturated compounds (A) may contain one or more olefinic double bonds. They may be low molecular weight (monomeric) or higher molecular weight (oligomeric). Examples of monomers having a double bond are alkyl and hydroxyalkyl acrylates and methacrylates, e.g. methyl, ethyl, butyl, 2-ethylhexyl and 2-hydroxyethyl acrylate, isobornyl acrylate and methyl and ethyl methacrylate. Also of interest are silicone acrylates. Further examples are acrylonitrile, acrylamide, methacrylamide, N-substituted (meth)acrylamides, vinyl esters, such as vinyl acetate, vinyl ethers, such as isobutyl vinyl ether, styrene, alkyl- and halo-styrenes, N-vinylpyrrolidone, vinyl chloride and vinylidene chloride.

Examples of monomers having a plurality of double bonds are ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, hexamethylene glycol diacrylate and bisphenol-A diacrylate, 4,4'-bis(2-acryloyloxyethoxy)diphenylpropane, trimethylolpropane triacrylate, pentaerythritol triacrylate and pentaerythritol tetraacrylate, vinyl acrylate, divinylbenzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate and tris(2-acryloylethyl)isocyanurate.

Examples of higher-molecular-weight (oligomeric) polyunsaturated compounds are acrylated epoxy resins, acrylated or vinyl-ether- or epoxy-group-containing polyesters, polyurethanes and polyethers. Further examples of unsaturated oligomers are unsaturated polyester resins, which are usually produced from maleic acid, phthalic acid and one or more diols and have molecular weights of about from 500 to 3000. In addition it is also possible to use vinyl ether monomers and oligomers, and also maleate-terminated oligomers having polyester, polyurethane, polyether, polyvinyl ether and epoxide main chains. Combinations of vinyl-ether-group-carrying oligomers and polymers, as described in WO 90/01512, are especially suitable, but copolymers of monomers functionalised with vinyl ether and maleic acid also come into consideration. Such unsaturated oligomers can also be termed prepolymers.

trimethylolpropane triacrylate, trimethyloethane triacrylate, trimethylolpropane trimethacrylate, trimethyloethane trimethacrylate, tetramethylene glycol dimethacrylate, triethylene glycol

Suitable unsaturated polyesters and polyamides are derived, for example, from maleic acid and diols or diamines. The maleic acid may have been partially replaced by other dicarboxylic acids. They may be used together with ethylenically unsaturated comonomers, e.g. styrene. The polyesters and polyamides may also be derived from dicarboxylic acids and ethylenically unsaturated diols or diamines, especially from those having longer chains of e.g. from 6 to 20 carbon atoms. Examples of polyurethanes are those composed of saturated diisocyanates and unsaturated diols or unsaturated diisocyanates and saturated diols.

The unsaturated compounds can also be used in admixture with non-photopolymerisable film-forming components. These may be, for example, polymers that can be dried physically or solutions thereof in organic solvents, for example nitrocellulose or cellulose acetobutyrate,

but they may also be chemically or thermally curable resins, for example polyisocyanates, polyepoxides or melamine resins. The concomitant use of thermally curable resins is important for use in so-called hybrid systems, which are photopolymerised in a first step and cross-linked by thermal after-treatment in a second step.

The photoinitiator suspensions according to the invention are also suitable as initiators for the curing of oxidatively drying systems, as described, for example, in *Lehrbuch der Lacke und Beschichtungen* Volume III, 296-328, Verlag W.A. Colomb in der Heenemann GmbH, Berlin-Oberschwandorf (1976).

Preferably, the aqueous photoinitiator suspensions according to the invention are used as photoinitiators in aqueous formulations that are to be polymerised.

The invention accordingly relates also especially to compositions comprising as component (A) at least one ethylenically unsaturated photopolymerisable compound dissolved or emulsified in water.

Such aqueous radiation-curable prepolymer dispersions are commercially available in many variations and are described in the literature. They are to be understood as being dispersions consisting of water and at least one prepolymer dispersed therein. The concentration of water in such systems is, for example, from 5 to 80% by weight, especially from 30 to 60% by weight. The radiation-curable prepolymer or mixture of prepolymers is present, for example, in concentrations of from 95 to 20% by weight, especially from 70 to 40% by weight. In such compositions, the sum of the percentages mentioned for water and prepolymer will be 100 in each case, the auxiliaries and additives, which will be present in varying amounts in accordance with the intended use, being in addition thereto.

The radiation-curable film-forming prepolymers, which are dispersed or in many cases dissolved in water, are mono- or poly-functional ethylenically unsaturated prepolymers such as, for example, are described above, that can be initiated by free radicals and are known *per se* for aqueous prepolymer dispersions, and that contain, for example, from 0.01 to 1.0 mol of polymerisable double bonds per 100 g of prepolymer and have an average molecular weight of, for example, at least 400, especially of from 500 to 10 000. Prepolymers having higher molecular weights may also be suitable, however, depending upon the intended use.

There are used, for example, polymerisable C-C double-bond-containing polyesters having an acid number of a maximum of 10, polymerisable C-C double-bond-containing polyethers, hydroxy-group-containing reaction products of a polyepoxide containing at least two epoxy groups per molecule with at least one α,β -ethylenically unsaturated carboxylic acid, poly-

The photopolymerisable mixtures may also contain various additives (C) in addition to the photoinitiator (B). Examples thereof are thermal inhibitors, which are intended to prevent premature polymerisation, e.g. hydroquinone, hydroquinone derivatives, p-methoxyphenol, β -naphthol or sterically hindered phenols, e.g. 2,6-di(tert-butyl)-p-cresol. In order to increase dark-storage stability it is possible to use, for example, copper compounds, such as copper naphthenate, stearate or octoate, phosphorus compounds, for example triphenylphosphine, tributylphosphine, triethyl phosphite, triphenyl phosphite or tribenzyl phosphite, quaternary ammonium compounds, e.g. tetramethylammonium chloride or trimethylbenzylammonium

chloride, or hydroxylamine derivatives, e.g. N-diethylhydroxylamine. For the purpose of excluding atmospheric oxygen during polymerisation it is possible to add paraffin or similar wax-like substances which, being insoluble in the polymer, migrate to the surface at the beginning of the polymerisation and form a transparent surface layer which prevents air from entering. Equally possible is the application of a layer that is impermeable to oxygen. As light stabilisers it is possible to add UV absorbers, e.g. those of the hydroxyphenylbenzotriazole, hydroxyphenylbenzophenone, oxalic acid amide or hydroxyphenyl-s-triazine type. Such compounds can be used on their own or in the form of mixtures, with or without the use of sterically hindered amines (HALS).

The following are examples of such UV absorbers and light stabilisers:

1. 2-(2'-Hydroxyphenyl)-benzotriazoles, e.g. 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)-phenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)-benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)-benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)-benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)-benzotriazole, a mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)-phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)-phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)-phenyl)-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)-phenyl)-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)-benzotriazole and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)-phenyl)-benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-yl-phenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_2$ wherein R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-yl-phenyl.
2. 2-Hydroxybenzophenones, e.g. a 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy or 2'-hydroxy-4,4'-dimethoxy derivative.
3. Esters of unsubstituted or substituted benzoic acids, e.g. 4-tert-butyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)-resorcinol, benzoylresorcinol, 3,5-di-tert-butyl-4-hydroxybenzoic acid 2,4-di-tert-butylphenyl ester, 3,5-di-tert-butyl-4-hydroxybenzoic acid hexadecyl ester, 3,5-di-tert-butyl-4-hydroxy-

benzoic acid octadecyl ester and 3,5-di-tert-butyl-4-hydroxybenzoic acid 2-methyl-4,6-di-tert-butylphenyl ester.

4. Acrylates, e.g. α -cyano- β,β -diphenylacrylic acid ethyl ester or isooctyl ester, α -methoxycarbonylcinnamic acid methyl ester, α -cyano- β -methyl-p-methoxycinnamic acid methyl ester or butyl ester, α -methoxycarbonyl-p-methoxycinnamic acid methyl ester and N-(β -methoxycarbonyl- β -cyanovinyl)-2-methyl-indoline.

5. Sterically hindered amines, e.g. bis(2,2,6,6-tetramethylpiperidyl)sebacate, bis(2,2,6,6-tetramethylpiperidyl)succinate, bis(1,2,2,6,6-pentamethylpiperidyl)sebacate, n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonic acid bis(1,2,2,6,6-pentamethylpiperidyl) ester, the condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetraoate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensation product of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensation product of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)-pyrrolidine-2,5-dione and 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)-pyrrolidine-2,5-dione.

6. Oxalic acid diamides, e.g. 4,4'-dioctyloxy-oxanilide, 2,2'-diethoxy-oxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyl oxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyl oxanilide, 2-ethoxy-2'-ethyl oxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyl oxanilide and a mixture thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyl oxanilide and mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

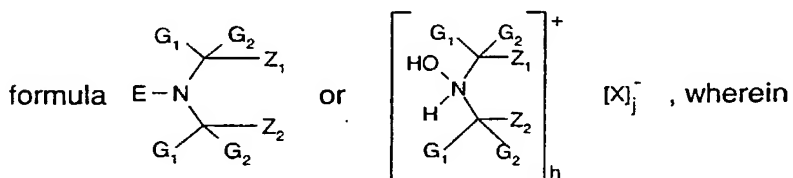
7. 2-(2-Hydroxyphenyl)-1,3,5-triazines, e.g. 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-

methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propyloxy)-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-[4-dodecyloxy/tridecyloxy-(2-hydroxypropyl)oxy-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

8. Phosphites and phosphonites, e.g. triphenyl phosphite, diphenylalkyl phosphites, phenyl-dialkyl phosphites, tris(nonylphenyl)phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl-pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecylpentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, bis-isodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl)-pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite.

Also of interest in this connection are, especially, water-soluble NOR-HALS stabiliser compounds, which can be incorporated as additives into the photoinitiator suspension according to the invention directly, or can be added as additives to the polymerisable mixtures.

Examples of such water-soluble NOR-HALS stabiliser compounds are derivatives of 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol and their hydroxylamine salts, for example compounds of



G_1 and G_2 are each independently of the other C_1 - C_4 alkyl or are together pentamethylene; Z_1 and Z_2 are each methyl, or Z_1 and Z_2 together form a linking group that may additionally be substituted by an ester, ether, hydroxy, oxo, cyanohydrin, amide, amino, carboxy or urethane group;

E is oxyl; hydroxy; hydrogen; alkyl; alkyl substituted by hydroxy, oxo or carboxy or interrupted by oxygen or carboxy; alkenyl; alkynyl; cycloalkyl; cycloalkenyl; bicycloalkyl; alkoxy; alkoxy substituted by hydroxy, oxo or carboxy or interrupted by oxygen or carboxy; cycloalkoxy; al-

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate; bis(1-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate; 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidinium citrate; 1-oxyl-2,2,6,6-tetramethyl-4-acetamidopiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium bisulfate; 1-oxyl-2,2,6,6-tetramethyl-4-oxo-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-oxo-piperidinium acetate; 1-oxyl-2,2,6,6-tetramethyl-4-methoxy-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-methoxy-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-methoxy-piperidinium acetate; 1-oxyl-2,2,6,6-tetramethyl-4-acetoxypiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-acetoxypiperidine; 1-oxyl-2,2,6,6-tetramethyl-4-propoxy-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidinium acetate; 1-hydroxy-2,2,6,6-tetramethyl-4-propoxy-piperidine; 1-oxyl-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentyloxy)-piperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-(2-hydroxy-4-oxapentyloxy)piperidinium acetate; 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine; 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium chloride; 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium acetate; 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium bisulfate; 1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium citrate; bis(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)citrate; tris(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)citrate; tetra(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)-ethylenediamine tetraacetate; tetra(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)-ethylenediamine tetraacetate; tetra(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)-ethylenediamine tetraacetate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)-diethylenetriamine pentaacetate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)diethylenetriamine pentaacetate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)diethylenetriamine pentaacetate; tri(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)nitrilotriacetate; tri(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)nitrilotriacetate; tri(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)nitrilotriacetate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidinium)diethylenetriamine pentamethylene phosphonate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-acetamidopiperidinium)diethylene-

triamine pentamethylenephosphonate; penta(1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidinium)diethylenetriamine pentamethylenephosphonate.

Also advantageous is the addition of biocides, as further additives (C), to the compositions according to the invention. Compounds known to the person skilled in the art and customary in the art are suitable. Examples include chloroacetamide, formalin and 1,2-benzoisothiazolin-3-one or also fungicides. The biocides are added, for example, in an amount of from 0.05 to 0.5% by weight.

The biocides can also be added directly to the above-described photoinitiator dispersion according to the invention and incorporated with that dispersion into the composition to be polymerised.

Additives customary in the art, such as, for example, antistatic agents, flow improvers and adhesion promoters, may also be used.

In order to accelerate the photopolymerisation, there may be added as further additives (C) amines, such as, for example, triethanolamine, N-methyl-diethanolamine, p-dimethylamino-benzoic acid ethyl ester or Michler's ketone. The action of the amines can be enhanced by the addition of aromatic ketones of the benzophenone type. Amines suitable for use as oxygen capture agents are, for example, substituted N,N-dialkylanilines, as described in EP 339 841. Further accelerators, co-initiators and auto-oxidisers are thiols, thioethers, disulfides and phosphines, as described e.g. in EP 438 123 and GB 2 180 358.

It is also possible to add chain transfer reagents customary in the art to the compositions according to the invention. Examples include mercaptans, amines and benzothiazole.

Photopolymerisation can also be accelerated by the addition, as further additives (C), of photosensitisers that shift or broaden the spectral sensitivity. These include especially aromatic carbonyl compounds, e.g. benzophenone, thioxanthone, especially isopropylthioxanthone, anthraquinone and 3-acylcoumarin derivatives, terphenyls, styryl ketones, and also 3-(aroylmethylene)-thiazolines, camphorquinone, and also eosin, rhodamine and erythrosine dyes.

There may also be considered as photosensitisers, for example, the above-mentioned amines.

Depending upon the intended use, the pigments are added to the formulations in amounts customary in the art, for example in an amount of from 0.1 to 60% by weight, for example

from 1 to 60% by weight, e.g. from 10 to 50 or from 10 to 40% by weight, based on the total mass.

The formulations may also comprise, for example, organic dyes of an extremely wide variety of classes. Examples are azo dyes, methine dyes, anthraquinone dyes and metal complex dyes. Customary concentrations are, for example, from 0.1 to 20%, especially from 1 to 5% by weight, based on the total mass.

In certain cases it may be advantageous to use further known photoinitiators as further additives. Examples of such compounds are benzophenone, benzophenone derivatives, e.g. 2,4,6-trimethylbenzophenone, 2-methylbenzophenone, 3-methylbenzophenone, 4-methylbenzophenone, 4,4'-bis(chloromethyl)benzophenone, 4-chlorobenzophenone, 4-phenylbenzophenone, 3,3'-dimethyl-4-methoxy-benzophenone, [4-(4-methylphenylthio)phenyl]-phenylmethanone, methyl 2-benzoylbenzoate, acetophenone, acetophenone derivatives, e.g. α -hydroxycycloalkylphenyl ketone or 2-hydroxy-2-methyl-1-phenyl-propanone, dialkoxyacetophenone, α -hydroxy- or α -amino-acetophenone, e.g. (4-methylthiobenzoyl)-1-methyl-1-morpholino-ethane, (4-morpholino-benzoyl)-1-benzyl-1-dimethylaminopropane, 4-aryl-1,3-dioxolane, benzoin alkyl ethers and benzil ketal, e.g. benzil dimethyl ketal, phenyl glyoxalate and derivatives thereof, dimeric phenyl glyoxalates, further monoacylphosphine oxides, e.g. (2,4,6-trimethylbenzoyl)phenyl-phosphine oxide, (2,4,6-trimethylbenzoyl)ethoxy-phosphine oxide, further bisacylphosphine oxides, e.g. bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethyl-pent-1-yl)phosphine oxide, bis(2,4,6-trimethylbenzoyl)phenyl-phosphine oxide or bis(2,4,6-trimethylbenzoyl)-(2,4-dipentyloxyphenyl)phosphine oxide, trisacylphosphine oxides, ferrocenium compounds or titanocenes, e.g. dicyclopentadienyl-bis(2,6-difluoro-3-pyrrolophenyl)titanium.

When the photoinitiator suspensions according to the invention are used in systems that comprise both free-radically polymerisable and cationically polymerisable components, there are added to the suspensions according to the invention comprising free-radical hardeners, in addition, cationic photoinitiators, e.g. aromatic sulfonium, phosphonium or iodonium salts, as described, e.g. in US 4 950 581, column 18, line 60 to column 19, line 10, or cyclopentadienylarene-iron(II) complex salts, e.g. (η^6 -isopropylbenzene)(η^5 -cyclopentadienyl)iron(II) hexafluorophosphate. It is also possible for peroxides, e.g. benzoyl peroxide, to be added (other suitable peroxides are described in US 4 950 581, column 19, lines 17 to 25).

Unsaturated polyester resins are generally used in two-component systems together with a monounsaturated monomer, preferably styrene. For photoresists, specific one-component systems are often used, e.g. polymaleinimides, polychalcones or polyimides, as described in DE 2 308 830.

The photocurable compositions according to the invention are suitable, for example, as coating materials for all kinds of substrate, for example wood, textiles, paper, ceramics, glass, plastics, such as polyesters, polyethylene terephthalate, polyolefins and cellulose acetate, especially in the form of films, and also metals, such as Al, Cu, Ni, Fe, Zn, Mg or Co and GaAs, Si or SiO₂, to which a protective layer is to be applied or an image is to be applied by imagewise exposure.

The substrates can be coated by applying a liquid composition, a solution or a suspension to the substrate. The choice of solvent and concentration are governed chiefly by the nature of the composition and the coating method. The solvent should be inert, that is to say it should not enter into any chemical reaction with the components, and it should be capable of being removed again after the coating operation during drying. Suitable solvents include, for example, water, ketones, ethers and esters, such as methyl ethyl ketone, isobutyl methyl ketone, cyclopentanone, cyclohexanone, N-methylpyrrolidone, dioxane, tetrahydrofuran, 2-methoxyethanol, 2-ethoxyethanol, 1-methoxy-2-propanol, 1,2-dimethoxyethane, ethyl acetate, n-butyl acetate and ethyl 3-ethoxypropionate.

The formulation is applied uniformly to a substrate by means of known coating methods, for example by spin-coating, immersion, knife coating, curtain pouring, brush application or spraying, especially by electrostatic spraying and reverse-roll coating, or by electrophoretic deposition. It is also possible to apply the photosensitive layer to a temporary flexible support and then coat the final substrate, e.g. a copper-clad circuit board, by transferring the layer by lamination.

The amount applied (layer thickness) and nature of the substrate (layer support) depend upon the desired field of use. The layer thickness range generally includes values of, for example, from approximately 0.1 μm to more than 100 μm , or, for example, from 0.02 to 2 cm. Preferably, the photoinitiator suspensions according to the invention are used in aqueous surface-coating formulations. The layer thickness range for that application includes, for example, from 0.1 μm to 500 μm , especially from 1 μm to 200 μm .

As has already been mentioned, the compositions according to the invention can also be used to produce a photoresist, which is obtained by "imagewise" exposure, that is to say exposure using a photomask having a predetermined pattern, e.g. a transparency, or exposure

Aqueous photoinitiator suspensions according to the invention are also suitable as initiators in "dual-cure" processes. "Dual-cure" in this context is to be understood as the combination

The photosensitivity of the preferably aqueous photocurable compositions according to the invention usually extends from approximately 200 nm to approximately 600 nm (UV range). Suitable radiation, for example, comprises sunlight or light from artificial light sources. A large number of the most varied types of light source accordingly come into consideration for use. Both point sources and planiform radiators (lamp carpets) are suitable. Examples are: carbon arc lamps, xenon arc lamps, medium pressure, high pressure and low pressure mercury radiators, doped, where appropriate, with metal halides (metal halide lamps), microwave-excited metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon incandescent lamps, flash lamps, photographic floodlight lamps, light-emitting diodes (LED), electron beams and X-rays. The distance between the lamp and the substrate according to the invention to be exposed may vary according to the intended use and the type and strength of the lamp and may be, for example, from 2 cm to 150 cm. Also suitable are, for example, laser light sources, e.g. excimer lasers, such as Krypton-F lasers for exposure at 248 nm. Lasers in the visible range may also be used. Using this method, it is possible to produce printed circuits for the electronics industry, lithographic offset printing plates or relief printing plates, and also photographic image-recording materials.

The invention accordingly relates also to a process for the photopolymerisation of non-volatile monomeric, oligomeric or polymeric compounds having at least one ethylenically unsaturated double bond, which comprises irradiating a composition as described above with light in the range from 200 to 600 nm.

The invention relates also to the use of the above-described composition in, and to a process for, the production of surface coatings, printing inks, screen-printing inks, offset-printing inks, flexographic-printing inks, resist materials or image-recording material, especially for corresponding aqueous systems.

The invention relates likewise to a coated substrate that is coated on at least one surface with a composition as described above.

The following Examples further illustrate the invention. Unless otherwise indicated, parts and percentages, both in the remainder of the description and in the patent claims, relate to weight. When alkyl or alkoxy radicals having more than three carbon atoms are mentioned without reference to their isomeric form, the statements relate to the respective n-isomers.

Example 1: Preparation of an aqueous photoinitiator formulation (D1)

[40% bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, ^{RTM}IRGACURE 819, Ciba-Spezialitätenchemie AG; 4% dispersing agent, sodium salt of a carboxylic acid copolymer, ^{RTM}OROTAN 731 DP, Rohm + Haas Company; 0.1% bactericide, 1,2-benzisothiazol-3-one, ^{RTM}PROXEL BD, Novartis AG; 55.9% water (deionised)].

1.1 Preparation of the suspension

In a glass beaker with an anchor stirrer,

0.65 g of bactericide (^{RTM}PROXEL BD) and

26.00 g of dispersing agent (^{RTM}OROTAN DP 731) are dissolved in

363.40 g of deionised water at room temperature, with stirring.

260.0 g of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide are introduced into the resulting solution and the batch is stirred for approximately one hour, yielding 650 g of an aqueous suspension.

1.2 Preliminary grinding

At room temperature, the suspension obtained in accordance with Example 1.1 is preground by means of a cross-toothed colloid mill (stator-rotor principle, water-cooled; Fryma AG Ma-

schinenbau, Rheinfelden, Switzerland) three times in the pendulum procedure at the narrowest grinding gap setting. During the course of the operation the temperature of the suspension does not exceed 35°C. After the grinding operation the largest particles of the bisacylphosphine oxide have a diameter of approximately 60 micrometres.

1.3 Fine-grinding

An agitator ball mill (Bachofen KDL type having a 0.6 litre grinding cylinder) is filled with 82% by volume of glass beads having a diameter of 1 mm (= 500 g of glass beads based on the grinding cylinder contents) and the water-cooling of the mill is commenced. At room temperature, the preground aqueous suspension according to Example 1.2 is finely ground three times in the pendulum procedure by means of the agitator ball mill at a shaft speed of 2000 rpm. The throughput is approximately 8 litres of suspension/hour. The temperature of the grinding stock increases to a maximum of 32°C during the course of the procedure. The required degree of particle-size fineness is reached after the third grinding operation. The particle size distribution of the bisacylphosphine oxide in the suspension is ascertained using a laser granulometer. The 50% median value is approximately 2.5 micrometres; the largest particles have a diameter of approximately 12 micrometres. The result is a homogeneous formulation that flows well at room temperature, the storage stability of which at from 20° to 25°C is more than one month (that is to say, there is no sedimentation and no serum formation).

Example 2: Preparation of an aqueous photoinitiator formulation (D2)

[40% bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, ^{RTM}IRGACURE 819, Ciba Spezialitätenchemie AG; 4% dispersing agent, polyvinyl alcohol with a degree of saponification of 88 mol %, ^{RTM}MOWIOL 8-88, Hoechst AG; 0.1% bactericide, 1,2-benzisothiazol-3-one, ^{RTM}PROXEL BD, Novartis AG; 55.9% water (deionised)]

In a plane-ground flask fitted with an anchor stirrer,

0.65 g of bactericide, (^{RTM}PROXEL BD) and
26.00 g of dispersing agent (^{RTM}MOWIOL 8-88) are introduced, with stirring, into
363.40 g of deionised water.

By heating to 65°C and maintaining at that temperature for approximately 30 minutes, with gentle stirring, a solution is obtained. After cooling the solution to 25°C while stirring slowly,

260.0 g of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide are introduced. The resulting mixture is stirred at room temperature for approximately one hour, yielding 650 g of an aqueous suspension.

The preliminary grinding and the fine grinding are carried out as described in Example 1 (1.2-1.3).

Example 3: Preparation of an aqueous photoinitiator formulation (D3)

- 33.0% of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (^{RTM}IRGACURE 819, Ciba Spezialitätenchemie),
- 33.0% of modified polyacrylate as dispersing agent (^{RTM}EFKA 4550, efka Chemicals, Netherlands),
- 33.0% of deionised water,
- 0.3% of antifoam (^{RTM}BYK 023, Byk Chemie)

The components are mixed by shaking with glass beads in a disperser. For that purpose the components are introduced into a glass vessel and glass beads of 1 mm diameter (1 to 2 times the total mass of the formulation) are added thereto. The volume of the glass vessel is such that approximately 30% of the total volume is not filled (formulation volume/glass beads volume/air volume = 1:1:1). This grinding batch is dispersed for 1 hour on an oscillatory shaking machine according to ISO 8780-3 : 1990 (Skandex SM-5, Lau GmbH, Germany).

Example 4: Preparation of an aqueous photoinitiator formulation (D4)

- 50.0% of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (^{RTM}IRGACURE 819, Ciba Spezialitätenchemie),
- 25.0% of modified polyacrylate as dispersing agent, (^{RTM}EFKA 4550, efka Chemicals, Netherlands),
- 25.0% of deionised water,
- 0.3% of antifoam (^{RTM}BYK 023, Byk)

The components are mixed as described in Example 3.

Example 5: Curing of an aqueous white surface coating

A white surface-coating formulation is prepared by mixing together the following components at room temperature:

- 55.8% of a neutralised, monomer-free and solvent-free acrylic- and urethane-modified polyether (^{RTM}VIAKTIN VTE 6155w/50WA, Vianova Resins AG)
- 3.3% of an alkyd resin in the form of a paste with butyl glycol and solvent naphtha 150/180 (^{RTM}ADDITOL XL 280, Vianova Resins AG)
- 10.2% of water

- 27.9% of rutile titanium dioxide (^{RTM}KRONOS 2310, Kronos)
- 0.4% of flow agent (^{RTM}BYK 307, Byk Chemie)
- 0.4% of flow agent (^{RTM}BYK 348, Byk Chemie)
- 2.0% of photoinitiator (based on the binder formulation with water content)

The 2% photoinitiator is composed of 1.6% 1-benzoyl-1-hydroxy-1-methyl-ethane (^{RTM}DAROCUR 1173, Ciba Spezialitätenchemie) and 0.4% bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, (^{RTM}IRGACURE 819, Ciba Spezialitätenchemie) as component of the aqueous formulations mentioned in Examples 2 and 3.

Layers are applied using a 100 µm slotted knife to chipboard panels that have been coated with a light-coloured primer, and the layers are dried for 10 minutes at 40°C and cured using two 80 W/cm medium-pressure mercury lamps at a belt speed of 10 m/min in a UV exposure apparatus from AETEK. The pendulum hardness according to König (DIN 53157), the yellowness index (ASTMD 1925-88) and the gloss (ASTMD 532) of the cured and wipe-resistant layers are determined. The yellowness index value of the uncoated chipboard panel is 5.0. The results are represented in the following Table 1.

Table 1

2% photoinitiator	pendulum hardness [sec]	yellowness index	gloss (20°/60°)
1-benzoyl-1-hydroxy-1-methyl-ethane + initiator D2	97	6.0	50/85
1-benzoyl-1-hydroxy-1-methyl-ethane + initiator D3	83	5.6	55/87

Example 6: Photopolymerisation in aqueous solution

1% bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (as component of the aqueous formulations mentioned in Examples 1 to 4) is used to photopolymerise a 50% aqueous acrylamide solution or the ammonium salt of acrylic acid (acrylic acid neutralised with 25% ammonium hydroxide solution).

A 20 g specimen is irradiated, with gentle rotation, under TL 40/03 fluorescent tubes (Philips). The irradiation time is registered after the reaction mass has gelled. The results are illustrated in the following Table 2.

Layers are applied using a 100 µm slotted knife to chipboard panels that have been coated with a light-coloured primer and the layers are dried at room temperature overnight. The chipboard panels are stored in an inclined position in outside light for a few hours (Basle, May) The pendulum hardness values according to König (DIN 53157) are measured before (0) and after 30 minutes and after 3 hours of curing with outside light. In all cases a significant increase in hardness can already be detected after 30 minutes. The results are shown in the following Table 3.

Table 3

formulation	pendulum hardness [sec] after		
	0 min	30 min	3 h
A	13	84	78
B	32	67	68
C	24	62	73
D	15	36	56
E	18	52	54
F	14	39	42

Example 8: Curing of a wood coating, with the addition of light stabilisers, using outside light 1% of the photoinitiator formulation mentioned in Example 1 (D1) and 1% of the UV absorber UV-1¹ (RTM-TINUVIN 1130, Ciba Spezialitätenchemie) are added to the aqueous binder dispersion A. The coatings are applied to a spruce-wood board using a paintbrush.

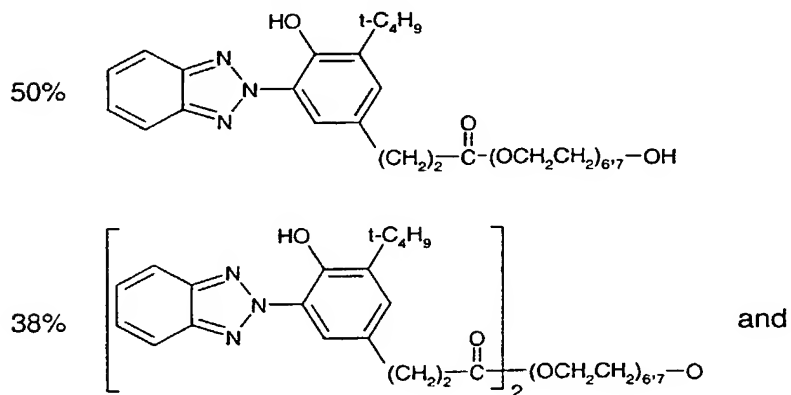
In a further test, before the application of formulation A the board is pretreated with a 1% aqueous solution of a sterically hindered amine-N-oxide.

After storage for 6 days in outside light (as described in Example 7), the yellowness index is measured.

An uncoated board (unexposed and exposed to light) and a coating comprising the aqueous binder dispersion A (with and without the photoinitiator formulations mentioned in Example 1) serve as references.

The results obtained are given in the following Table 4.

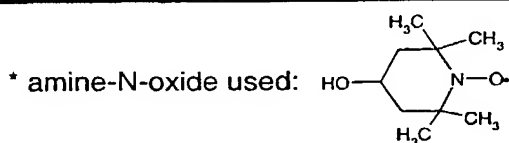
¹ The UV absorber UV-1 is a mixture of



12% polyethylene glycol 300.

Table 4

Specimen	YI
uncoated and unexposed	43.7
uncoated and exposed	64.1
coated with A	64.7
coated with A + 1% initiator from Example 1 (D1)	63.0
coated with A + 1% initiator from Example 1 (D1) + 1% UV absorber	52.2
pretreated with 1% aqueous amine-N-oxide solution*	
coated with A + 1% initiator from Example 1 (D1) + 1% UV absorber	43.9



Example 9: Curing of an aqueous hybrid system with outside light

This Example is concerned with mixtures of a component that can be dried physically (aqueous emulsion of an anionic acrylic copolymer, ^{RTM}GLASCOL C36, Ciba Spezialitäten-chemie AG) and a photocurable component (aqueous binder dispersion A).

The test formulations are listed in the following Table 5. In each case 1% of the aqueous photoinitiator formulation according to Example 1 (D1) is admixed with the formulations comprising photoinitiator. Formulations of the pure binders with and without photoinitiator are used as references.

Curing with outside light is carried out as described in Example 8. After curing, the resistance to solvents is tested using a cube of felt impregnated with ethanol. The cube of felt is left lying on the surface-coating layer, under a cover, overnight and then the condition of the layer is evaluated in the following manner:

- + = no attack
- = slight attack
- = appreciable attack
- = layer totally dissolved.

The results are given in Table 5.

Table 5

components of the mixture			ethanol test
A	^{RTM} GLASCOL C36	initiator	
100%	0	0	- - -
100%	0	1%	+
0	100%	0	- -
0	100%	1%	- -
25%	75%	0	-
25%	75%	1%	+
50%	50%	0	-
50%	50%	1%	+

Example 10: Curing of an aqueous "dual-cure" system

A formulation is prepared from

- 36.2 parts of polyacrylate (^{RTM}BAYHYDROL VP LS 2271, Bayer)
- 0.3 part of flow agent (^{RTM}BYK 345, Byk Chemie)
- 0.3 part of flow agent (^{RTM}BYK 333, Byk Chemie)
- 16.9 parts of deionised water
- 52.6 parts of a urethane acrylate having isocyanate groups (^{RTM}ROSKYDAL FWO 2545 E, Bayer)
- 8.9 parts of trimethylolpropane triacrylate (UCB), and
- 9.3 parts of 1-methoxy-2-propanol (Fluka).

2% of a photoinitiator mixture is added to the formulation. The photoinitiator mixture is composed of 87.5% 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one (^{RTM}IRGACURE 2959, Ciba Spezialitätenchemie) (PI-1) and in each case 12.5% of an aqueous photoinitiator formulation according to one of Examples 1-4 (D1-D4).

In addition, 1% of the UV absorber UV-2² (^{RTM}TINUVIN 400, Ciba Spezialitätenchemie) and 0.6% of the sterically hindered amine HALS-1³ (^{RTM}TINUVIN 292, Ciba Spezialitätenchemie) are added to some of the mixtures.

Layers are applied to coil-coated aluminium sheets using a 100 µm spiral knife and the layers are then dried for 5 minutes at room temperature and subsequently for 10 minutes by heating to 80°C. Exposure is then carried out at a belt speed of 5 m/min using two 120 W/cm medium-pressure mercury lamps.

A wipe-resistant layer is obtained, the pendulum hardness (PH) of which is measured 45 minutes after curing. The results are given in the following Table 6.

² The active substance of the UV absorber UV-2 is a mixture of 2-[4-[(2-hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-[4-[(2-hydroxy-3-tridecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine

³ The sterically hindered amine HALS-1 is a mixture of bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (Chem. Abstr. No. 41556-26-7) and methyl(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (Chem. Abstr. No. 82919-37-7).

Table 6

photoinitiator	UV-2/HALS-1	PH [sec.]
PI-1 + D1	without	39
PI-1 + D2	without	39
PI-1 + D3	without	36
PI-1 + D4	without	41
PI-1 + D1	with	38
PI-1 + D2	with	31
PI-1 + D3	with	36
PI-1 + D4	with	38

Example 11: Curing of an aqueous white surface-coating formulation

Various photoinitiator dispersions are incorporated into an aqueous white surface-coating formulation as described in Example 5, and the formulations are applied and cured as described in Example 5. The 2% photoinitiators are composed of 1.6% 1-benzoyl-1-hydroxy-1-methyl-ethane (^{RTM}DAROCUR 1173, Ciba Spezialitätenchemie) and 0.4% mono- or bis-acylphosphine oxide as component of an aqueous dispersion. After curing, the pendulum hardness of the coating is measured. The photoinitiator dispersions used (prepared analogously to the method described in Example 3) are given in Table 7a, and the curing results in Table 7b.

Table 7a

constituents	photoinitiator formulation [#]		
	D4	D5	D6
bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide	33	43	-
2,4,6-trimethylbenzoyl-diphenylphosphine oxide (^{RTM} LUCIRIN TPO, BASF AG)	-	-	43
modified polyacrylate as dispersing agent (^{RTM} EFKA 4550, efka Chemicals, Netherlands)	33	14	14
deionised water	33	43	43
antifoam (^{RTM} BYK 023, Byk Chemie)	0.3	0.4	0.4

figures in parts

Table 7b

photoinitiator formulation	pendulum hardness [s]
D4	105
D5	83
D6	20

Example 12: Curing of a non-aqueous white surface-coating formulation

A formulation is prepared from

- 74.0 parts of an unsaturated polyester, comprising 36% styrene (^{RTM}ROSKYDAL S502, Bayer AG)
- 24.5 parts of titanium dioxide (^{RTM}RTC2, Tioxide, France)
- 0.5 part of flow agent (^{RTM}BYK 300)
- 1.0 part of photoinitiator

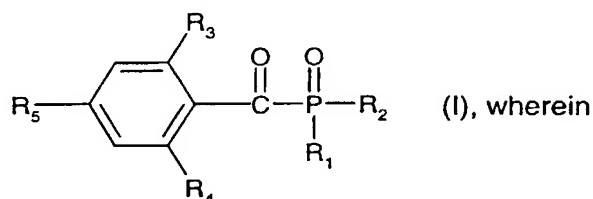
The photoinitiator is added in the form of a dispersion (D7), prepared analogously to the method described in Example 3, containing

- 45.0 parts of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (^{RTM}IRGACURE 819, Ciba Spezialitätenchemie, Switzerland)
- 4.5 parts of dispersing agent (^{RTM}OROTAN DP 731, Rohm & Haas)
- 0.1 part of bactericide: 1,2-benzisothiazol-3-one (^{RTM}PROXEL BD, Novartis)

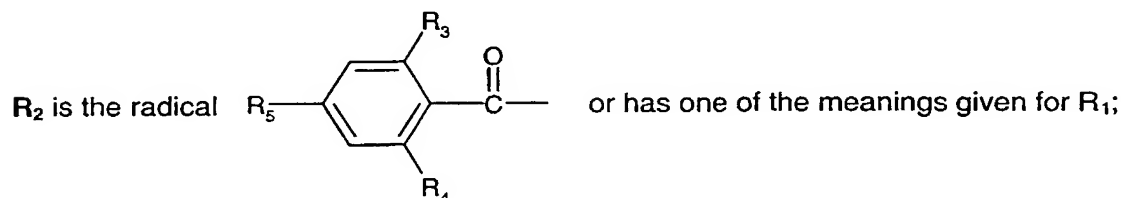
photoinitiator formulation	pendulum hardness [sec]	yellowness index	gloss (20°/60°)
D7	95	3.5	81/94

What is claimed is :

1. An aqueous, storage-stable, non-sedimenting suspension comprising
(a) at least one mono- or bis-acylphosphine oxide of formula I



R_1 is C_1 - C_{20} alkyl; C_2 - C_{20} alkyl interrupted by one or more O atoms; C_1 - C_{12} alkoxy; phenyl- C_1 - C_4 alkyl; or phenyl that is unsubstituted or substituted by C_1 - C_{20} alkyl, C_1 - C_{12} alkoxy, halogen, cyclopentyl, cyclohexyl, C_2 - C_{12} alkenyl, C_2 - C_{18} alkyl interrupted by one or more O atoms, and/or by phenyl- C_1 - C_4 alkyl; or R_1 is biphenyl;

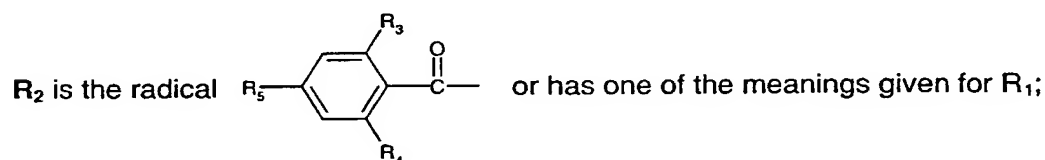


R_3 and R_4 are each independently of the other C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy or halogen; and
 R_5 is hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy or halogen;

- (b) at least one dispersant;
- (c) water; and, optionally,
- (d) further additives.

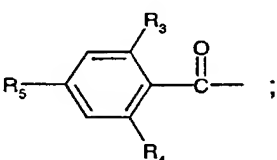
2. An aqueous suspension according to claim 1, comprising as component (a) a compound of formula I, wherein

R_1 is C_1 - C_{20} alkyl; C_1 - C_4 alkoxy; or phenyl that is unsubstituted or substituted by C_1 - C_{12} alkyl, C_1 - C_{12} alkoxy and/or by halogen;



R_3 and R_4 are each independently of the other C_1 - C_4 alkyl or C_1 - C_4 alkoxy; and R_5 is hydrogen, C_1 - C_{12} alkyl or C_1 - C_{12} alkoxy.

3. An aqueous suspension according to claim 1, comprising as component (a) bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide;
bis(2,4,6-trimethylbenzoyl)-2,4-dipentylphosphine oxide;
bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide; or
2,4,6-trimethylbenzoyldiphenylphosphine oxide.
4. An aqueous suspension according to claim 1, wherein the particle size of the solid or solids in the suspension is from 0.1 μm to 12 μm , especially from 0.1 μm to 4 μm .
5. An aqueous suspension according to claim 1, comprising from 10 to 80 parts of component (a);
from 1 to 40 parts of component (b); and
a sufficient number of parts of component (c) for the total composition to amount to 100 parts.
6. An aqueous suspension according to claim 1, comprising as component (b) polymers based on maleic acid anhydride, polyvinyl alcohol or modified polyacrylates, especially the alkali salts of carboxylic acid copolymers or polyvinyl alcohol.
7. An aqueous suspension according to claim 1, comprising

(a) a compound of formula I, wherein R_1 is phenyl or C_1 - C_{12} alkyl; R_2 is  ;

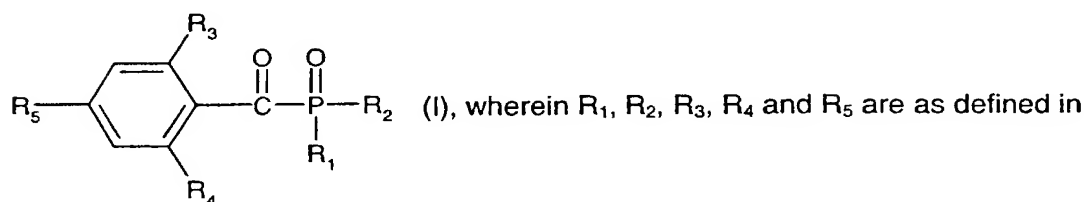
R_3 and R_4 are C_1 - C_4 alkyl or C_1 - C_4 alkoxy; and R_5 is hydrogen or C_1 - C_4 alkyl; and
(b) as dispersant, an alkali salt of a carboxylic acid polymer, polyvinyl alcohol or a modified polyacrylate.

8. An aqueous suspension according to claim 1, comprising as additional component (d) at least one biocide.

9. An aqueous suspension according to claim 1, comprising as additional component (d) at least one UV absorber and/or a sterically hindered amine.

10. A process for the preparation of an aqueous, storage-stable, non-sedimenting photoinitiator suspension comprising

(a) at least one mono- or bis-acylphosphine oxide of formula I



claim 1,

(b) at least one dispersant,

(c) water, and, optionally,

(d) further additives

by

(1) suspending components (a), (b) and (c) and, optionally, (d), by stirring;

(2) coarse-grinding the resulting mixture to a particle size of the solid material in the suspension of approximately 60 μm ; and

(3) fine-grinding the mixture by one or more grinding operations to a particle size of the solid material in the suspension of less than 12 μm .

11. A photopolymerisable composition comprising

(A) at least one ethylenically unsaturated photopolymerisable compound and

(B) as photoinitiator, a suspension according to claim 1.

12. A photopolymerisable composition according to claim 11, wherein component (A) comprises at least one ethylenically unsaturated photopolymerisable compound dissolved or emulsified in water.

13. A photopolymerisable composition according to claim 11, comprising in addition to components (A) and (B) further additives (C), especially from the group consisting of UV absorbers, sterically hindered amines, biocides and/or pigments.

14. A process for the photopolymerisation of compounds having ethylenically unsaturated double bonds, which comprises irradiating a composition according to claim 11 with light in the range from 200 to 600 nm.
15. A process according to claim 14 for the production of surface coatings, printing inks, screen-printing inks, offset-printing inks, flexographic-printing inks, resist materials or image-recording material, especially for the production of corresponding aqueous systems.
16. The use of an aqueous suspension according to claim 1 as photoinitiator in the photopolymerisation of compounds having ethylenically unsaturated double bonds.
17. The use of a composition according to claim 11 in the production of surface coatings, printing inks, screen-printing inks, offset-printing inks, flexographic-printing inks, resist materials or image-recording material, especially in the production of corresponding aqueous systems.
18. A coated substrate that is coated on at least one surface with a composition according to claim 11.

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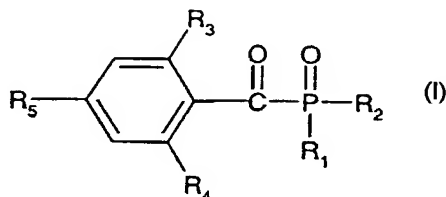
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(54) Title: PHOTOINITIATOR FORMULATIONS



(57) Abstract: Aqueous, storage-stable, non-sedimenting photoinitiator
suspensions comprising (a) a mono- or bis-acylphosphine oxide of formula
(I), wherein R₁ is C₁-C₂₀alkyl; C₂-C₂₀alkyl interrupted by one or more O
atoms; C₁-C₁₂alkoxy; phenyl-C₁-C₄alkyl; or phenyl that is unsubstituted or
substituted by C₁-C₂₀alkyl, C₁-C₁₂alkoxy, halogen, cyclopentyl, cyclohexyl,
C₂-C₁₂alkenyl, C₂-C₁₈alkyl interrupted by one or more O atoms, and/or by
phenyl-C₁-C₄alkyl; or R₁ is biphenyl; R₂ is an aromatic radical or has one
of the meanings given for R₁; R₃ and R₄ are each independently of the other
C₁-C₁₂alkyl, C₁-C₁₂alkoxy or halogen; and R₅ is hydrogen, C₁-C₁₂alkyl,
C₁-C₁₂alkoxy or halogen; (b) a dispersant; and (c) water are suitable especially in the photopolymerisation of aqueous formulations
comprising ethylenically unsaturated monomers.

US Case CO/2-22109/US/A

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☐ Original ☐ Supplemental ☐ Substitute ☒ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Photoinitiator formulations

which is described and claimed in:

- ☐ the attached specification.
- ☐ the specification in U.S. Application No. _____, and as amended on _____ (if applicable).
(day/month/year) (day/month/year)
- ☒ the specification in International Application No. **PCT/EP 00/10043**
filed **12/10/00**
(day/month/year)
- assigned U.S. Application No. _____ (if applicable), and as amended
- ☐ under PCT Article 19 on _____ (if applicable)
(day/month/year)
- ☐ under PCT Article 34 on _____ (if applicable)
(day/month/year)
- ☐ and further amended on _____ (if applicable)
(day/month/year)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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4056 Basel
Switzerland CHX

Citizenship Swiss

Post Office Address same as above

Full name of sixth
joint inventor, if any Martin HOLER

Inventor's signature Martin Holer Date 24.01.2002
(day/month/year)

Residence Hohle Gasse 70
4323 Wallbach
Switzerland CHX

Citizenship Swiss

Post Office Address same as above

Full name of seventh
joint inventor, if any Ernst ECKSTEIN

Inventor's signature Ernst Eckstein Date 25.1.2002
(day/month/year)

Residence Hinterm Holz 18
79618 Rheinfelden
Germany DEX

Citizenship German

Post Office Address same as above

US Case CO/2-22109/US/A

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATIONS

☐ Original ☐ Supplemental ☐ Substitute ☒ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if more than one name is listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Photoinitiator formulations

which is described and claimed in:

- ☐ the attached specification.
- ☐ the specification in U.S. Application No. _____, and as amended on _____ (if applicable).
(day/month/year) (day/month/year)
- ☒ the specification in International Application No. **PCT/EP 00/10043**
filed **12/10/00**
(day/month/year)
- assigned U.S. Application No. _____ (if applicable), and as amended
- ☐ under PCT Article 19 on _____ (if applicable)
(day/month/year)
- ☐ under PCT Article 34 on _____ (if applicable)
(day/month/year)
- ☐ and further amended on _____ (if applicable)
(day/month/year)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is known by me to be material to the patentability of this application as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America relating to this subject matter having a filing date before that of the application on which priority is claimed:

COUNTRY/REGION (OR PCT)	APPLICATION No.	FILING DATE (day/month/year)	PRIORITY CLAIMED	
Europe (designating DE)	99810953.2	20/10/99	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No
			<input type="checkbox"/> Yes	<input type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. § 119 (e) of any United States provisional application(s) listed below:

APPLICATION NO.	FILING DATE (day/month/year)
-----------------	---------------------------------

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or PCT international application(s) designating the United States listed below and, insofar as the application discloses and claims subject matter in addition to that disclosed in the prior copending application, I acknowledge the duty to disclose all information known by me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. APPLICATION No.	FILING DATE (day/month/year)	STATUS		
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned

PCT APPLICATION No. (designating the U.S.)	INTERNATIONAL FILING DATE (day/month/year)	U.S. APPLICATION No. (if any)	STATUS
			<input type="checkbox"/> Patented
			<input type="checkbox"/> Pending
			<input type="checkbox"/> Abandoned

I hereby appoint the following attorneys and agents, associated with Customer No. 000324, each of them with full power of substitution, revocation and appointment of associates, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Luther A. R. Hall (Reg. No. 27,337), JoAnn L. Villamizar (Reg. No. 30,598), Kevin T. Mansfield (Reg. No. 31,635), David R. Crichton (Reg. No. 37,300), Michele A. Kovaleski (Reg. No. 37,865) and Tyler A. Stevenson (Reg. No. 46,388).

Address all correspondence associated with Customer No. 000324 to ***Ciba Specialty Chemicals Corporation, Patent Department, 540 White Plains Road, P.O. Box 2005, Tarrytown, NY 10591-9005.***

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole
or first joint inventor **Manfred KÖHLER (deceased)**

Inventor's signature _____ Date _____
(day/month/year)

Residence **Kehler Strasse 15
79108 Freiburg
Germany**

Citizenship **German**

Post Office Address same as above

Full name of second
joint inventor, if any

Vivian KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

Kehler Strasse 15
79108 Freiburg
Germany

Citizenship

Ghanaian

Post Office Address

same as above

Full name of third
joint inventor, if any

Inga KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

Ebelingstrasse 7
10249 Berlin
Germany

Citizenship

German

Post Office Address

same as above

Full name of fourth
joint inventor, if any

Antoin Kamran KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

Kehler Strasse 15
79108 Freiburg
Germany

Citizenship

German

Post Office Address

same as above

Full name of fifth
joint inventor, if any **Beat Michael AEBLI**

Inventor's signature _____ Date _____
(day/month/year)

Residence **Lothringerstrasse 1**
4056 Basel
Switzerland

Citizenship **Swiss**

Post Office Address same as above

Full name of sixth
joint inventor, if any **Martin HOLER**

Inventor's signature _____ Date _____
(day/month/year)

Residence **Hohle Gasse 70**
4323 Wallbach
Switzerland

Citizenship **Swiss**

Post Office Address same as above

Full name of seventh
joint inventor, if any **Ernst ECKSTEIN**

Inventor's signature _____ Date _____
(day/month/year)

Residence **Hinterm Holz 18**
79618 Rheinfelden
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Citizenship **German**

Post Office Address same as above

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Photoinitiator formulations

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			<input type="checkbox"/> Yes	<input type="checkbox"/> No
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		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented	<input type="checkbox"/> Pending	<input type="checkbox"/> Abandoned

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(day/month/year)

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79108 Freiburg
Germany**

Citizenship **German**

Post Office Address same as above

Full name of second
joint inventor, if any

Vivian KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

**Kehler Strasse 15
79108 Freiburg
Germany**

Citizenship

Ghanaian

Post Office Address

same as above

Full name of third
joint inventor, if any

Inga KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

**Ebelingstrasse 7
10249 Berlin
Germany**

Citizenship

German

Post Office Address

same as above

Full name of fourth
joint inventor, if any

Antoin Kamran KÖHLER (legal representative of Manfred KÖHLER)

Inventor's signature

Date

(day/month/year)

Residence

**Kehler Strasse 15
79108 Freiburg
Germany**

Citizenship

German

Post Office Address

same as above

Full name of fifth
joint inventor, if any **Beat Michael AEBLI**

Inventor's signature _____ Date _____
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Residence **Lothringerstrasse 1**
4056 Basel
Switzerland

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Full name of sixth
joint inventor, if any **Martin HOLER**

Inventor's signature _____ Date _____
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Residence **Hohle Gasse 70**
4323 Wallbach
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Full name of seventh
joint inventor, if any **Ernst ECKSTEIN**

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79618 Rheinfelden
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Citizenship **German**

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